

BEST AVAILABLE COPY

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C04B</p>	<p>A2</p>	<p>(11) International Publication Number: WO 97/13732</p> <p>(43) International Publication Date: 17 April 1997 (17.04.97)</p>		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) International Application Number: PCT/US96/16232</p> <p>(22) International Filing Date: 11 October 1996 (11.10.96)</p> <p>(30) Priority Data: <div style="display: flex; justify-content: space-between;"> PCT/US95/13836 11 October 1995 (11.10.95) WO </div> <p>(34) Countries for which the regional or international application was filed: US et al.</p> <p>(60) Parent Application or Grant <div style="display: flex; justify-content: space-between;"> (63) Related by Continuation PCT/US95/13836 (CIP) </div> <div style="display: flex; justify-content: space-between;"> US 11 October 1995 (11.10.95) </div> <p>Filed on</p> <p>(71) Applicant: ALCELL TECHNOLOGIES INC. [CA/CA]; 1250 Rene-Levesque Boulevard West, Montreal, Quebec H3B 4W8 (CA).</p> </p></p></td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(71)(72) Applicants and Inventors: BREMNER, Theodore [CA/CA]; Youngs Cove Road, Jemsey, New Brunswick E0E 1F0 (CA). ZHOR, Jiri [CZ/CA]; Apartment 1, 321 University Avenue, Fredericton, New Brunswick E3B 4HN (CA). GOYAL, Gopal, C. [IN/US]; 1003 23rd Street, Cloquet, MN 55720 (US). LORA, Jairo, H. [CO/US]; 7 Camby Chase, Media, PA 19061 (US). CREAMER, Albert [US/US]; 22 Uphill Road, Levittown, PA 19056 (US).</p> <p>(74) Agents: HEIDELBERGER, Louis, M. et al.; Reed Smith Shaw & McClay, 2500 One Liberty Place, 1650 Market Street, Philadelphia, PA 19103 (US).</p> <p>(81) Designated States: CA, CN, JP, KR, NO, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p> </td> </tr> </table>			<p>(21) International Application Number: PCT/US96/16232</p> <p>(22) International Filing Date: 11 October 1996 (11.10.96)</p> <p>(30) Priority Data: <div style="display: flex; justify-content: space-between;"> PCT/US95/13836 11 October 1995 (11.10.95) WO </div> <p>(34) Countries for which the regional or international application was filed: US et al.</p> <p>(60) Parent Application or Grant <div style="display: flex; justify-content: space-between;"> (63) Related by Continuation PCT/US95/13836 (CIP) </div> <div style="display: flex; justify-content: space-between;"> US 11 October 1995 (11.10.95) </div> <p>Filed on</p> <p>(71) Applicant: ALCELL TECHNOLOGIES INC. [CA/CA]; 1250 Rene-Levesque Boulevard West, Montreal, Quebec H3B 4W8 (CA).</p> </p></p>	<p>(71)(72) Applicants and Inventors: BREMNER, Theodore [CA/CA]; Youngs Cove Road, Jemsey, New Brunswick E0E 1F0 (CA). ZHOR, Jiri [CZ/CA]; Apartment 1, 321 University Avenue, Fredericton, New Brunswick E3B 4HN (CA). GOYAL, Gopal, C. [IN/US]; 1003 23rd Street, Cloquet, MN 55720 (US). LORA, Jairo, H. [CO/US]; 7 Camby Chase, Media, PA 19061 (US). CREAMER, Albert [US/US]; 22 Uphill Road, Levittown, PA 19056 (US).</p> <p>(74) Agents: HEIDELBERGER, Louis, M. et al.; Reed Smith Shaw & McClay, 2500 One Liberty Place, 1650 Market Street, Philadelphia, PA 19103 (US).</p> <p>(81) Designated States: CA, CN, JP, KR, NO, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>
<p>(21) International Application Number: PCT/US96/16232</p> <p>(22) International Filing Date: 11 October 1996 (11.10.96)</p> <p>(30) Priority Data: <div style="display: flex; justify-content: space-between;"> PCT/US95/13836 11 October 1995 (11.10.95) WO </div> <p>(34) Countries for which the regional or international application was filed: US et al.</p> <p>(60) Parent Application or Grant <div style="display: flex; justify-content: space-between;"> (63) Related by Continuation PCT/US95/13836 (CIP) </div> <div style="display: flex; justify-content: space-between;"> US 11 October 1995 (11.10.95) </div> <p>Filed on</p> <p>(71) Applicant: ALCELL TECHNOLOGIES INC. [CA/CA]; 1250 Rene-Levesque Boulevard West, Montreal, Quebec H3B 4W8 (CA).</p> </p></p>	<p>(71)(72) Applicants and Inventors: BREMNER, Theodore [CA/CA]; Youngs Cove Road, Jemsey, New Brunswick E0E 1F0 (CA). ZHOR, Jiri [CZ/CA]; Apartment 1, 321 University Avenue, Fredericton, New Brunswick E3B 4HN (CA). GOYAL, Gopal, C. [IN/US]; 1003 23rd Street, Cloquet, MN 55720 (US). LORA, Jairo, H. [CO/US]; 7 Camby Chase, Media, PA 19061 (US). CREAMER, Albert [US/US]; 22 Uphill Road, Levittown, PA 19056 (US).</p> <p>(74) Agents: HEIDELBERGER, Louis, M. et al.; Reed Smith Shaw & McClay, 2500 One Liberty Place, 1650 Market Street, Philadelphia, PA 19103 (US).</p> <p>(81) Designated States: CA, CN, JP, KR, NO, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>			
<p>(54) Title: SULFOMETHYLOLATED LIGNIN-BASED CONCRETE ADMIXTURES</p> <p>(57) Abstract</p> <p>The invention provides for an admixture for reducing the water content of a concrete mix. The admixture comprises an alkaline solution of a lignin in a sulfomethylolated form. The sulfomethylolated lignin in the admixture can also be cross-linked with a cross-linking agent. The admixture further comprises an air detainer. Also provided are novel cement compositions comprising the admixture of the invention.</p>				

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

SULFOMETHYLOLATED LIGNIN-BASED CONCRETE ADMIXTURES5 BACKGROUND OF THE INVENTION

Cement compositions are brought into a workable form by mixing the solid components with an amount of water which is greater than that required to hydrate the cement components therein. The mixed mineral binder composition is poured into a form and allowed to harden at atmospheric temperature. During the hardening, some of the excess water remains, leaving cavities in the formed structural unit and, thus, reduces the mechanical strength of the resultant unit. It is well known that the compressive strength of the resultant structure generally bears an inverse relationship to the water-cement ratio of the starting mix. The need to use smaller quantities of water is limited by the required flow and workability properties of the fresh mixture.

20 In structural cement compositions, it is highly desirable to maintain very low water content in order to achieve high strength in the final product. However, since the amount of water needed for adequate workability of the cement exceeds that required by the chemistry of curing, this excess water results in weaker concrete.

Concrete admixtures refer to compounds and compositions added to concrete mixtures to alter their properties. Water-reducing agents have been used as concrete admixtures. They are generally used to improve workability while decreasing water addition so that a stronger and more durable concrete is obtained. Water-reducing agents are classified by their ability to reduce water content as superplasticizers or high-range water reducers and plasticizers or normal-range water reducers.

-2-

Plasticizers and superplasticizers are made using chemicals with surface-active characteristics. One of the traditional resources for the manufacture of water-reducing admixtures for concrete are the waste products from the pulp and paper industry, namely lignin and its derivatives. Traditionally, sulfite pulping has been the major source of lignosulfonates which after extended purification are used as normal range water-reducing and retarding admixtures for concrete. Attempts to use lignin-based methylsulphonates as water-reducing admixtures is known in the art as shown by "Effect of Chemical Characteristics of Alcell® Lignin-Based Methylsulphonates on Their Performance as Water-Reducing Admixtures", Superplasticizers and Other Chemical Admixtures in Concrete by J. Zhor, T. W. Bremner and J. H. Lora, 1994, incorporated by reference herein.

The chemical structure and composition of water-reducing admixtures influence their surfactant properties which generally determine their effectiveness in cement-water mixtures.

Lignin-type water-reducing agents are well known for use in preparing concrete mixes. Such agents serve to reduce the amount of water that would ordinarily be required to make a pourable mix, without however disturbing most of the other beneficial properties of the mix. On various occasions, however, the use of such water-reducing agents may entrain air into the mix. Entrained air (from any source) tends to reduce compressive strength. As a general rule, with every one volume percent air in the concrete, 5% of strength is lost. Thus, 5% air means about 25% strength loss. However, air entrainment may be desirable in certain applications such as the manufacture of concrete blocks.

-3-

Lignosulfonates are also known to slow down the curing of concrete thus causing what is known in the art as set retardation. Set retardation is particularly increased when the lignosulfonate contains impurities such as wood sugars.

5

Lignosulfonates are classified as anionic surfactants since the hydrophilic groups associated with the organic polymers are sulfonates. It has been reported that when absorbed onto cement particles, these surfactants impart a strong negative charge which lowers the surface tension of the surrounding water and greatly enhances the fluidity of the system. Lignosulfonates also exhibit set retarding properties. Lignosulfonates, when used in an amount sufficient to furnish the desired water reduction in a mix, normally entrain more air than desired and retard the setting time of concrete far beyond the ranges for a high-range water-reducing admixture.

Lignosulfonate-based concrete admixtures are usually prepared from the waste liquor formed by the production of sulfite pulp. By neutralization, precipitation and fermentation of this liquor a range of lignosulfonates of varying purity, composition and molecular weight distribution is produced. A number of researchers have reported several attempts to enhance the lignosulfonates so that they would meet the requirements of a superplasticizer as a high range water-reducing admixture. To date no purely lignosulfonate based superplasticizer for concrete has been placed on the market.

For example, in U.S. Pat. No. 4,239,550 is disclosed a flowing agent for concrete and mortar based on lignin sulfonate and on ring-sulfonated or sulfomethylolated aromatic substances. According to the invention, the flowing agent imparts to concrete or mortar high fluidity without leading to undesirably long setting times. In U.S. Pat. No. 4,460,720 is disclosed a superplasticizer cement admixture for portland cement based compositions formed from a low molecular weight alkali metal

-4-

poly-acrylate in combination with an alkali metal or alkaline earth metal poly-naphthalene sulfonate-formaldehyde or an alkali metal lignosulfonate or an alkaline earth metal lignosulfonate or mixtures thereof. In U.S. Pat. No. 4,623,682 is disclosed
5 cement mixes having extended workability without substantial loss in rate of hardening when containing an admixture combination of a sulfonated naphthalene-formaldehyde condensate and fractionated sulfonated lignin such as ultra-filtered lignosulfonate. In U.S. Pat. No. 4,351,671 is disclosed an
10 additive for lignin type water-reducing agent which reduces air entrainment in the concrete mix and in U.S. Pat. No. 4,367,094 is disclosed an agent for preventing deterioration in the slump properties of mortar concrete, containing as a main ingredient a lignin sulfonate.

15
Environmental considerations present an important aspect in the development of pulping technologies. Due to increasing environmental demands during the last three decades, traditional sulfite pulping has almost completely been replaced
20 by the kraft pulping process. Both sulfite and kraft pulping processes are noted for their contribution to air and water pollution, which requires costly pollution control equipment to bring kraft and sulfite pulping operations into environmental compliance. These pulping technologies can now be economically
25 replaced by more environmentally friendly processes. One of these processes is the organosolv pulping process which has minimal impact on the environment and produces a pure lignin as one of the coproducts to the pulp. Unlike the traditional sulfite process, the new organosolv pulping process allows for
30 the recovery of a pure, non-sulfonated form of lignin. This organosolv lignin can be suitable as a raw material for the preparation of a superplasticizer water-reducing admixtures for concrete.

35
By the methods of the present invention is provided an environmentally friendly organosolv lignin-based

-5-

superplasticizing and water-reducing admixture composition. The superplasticizer admixture compositions of the invention can impart a high degree of fluidity to cement compositions, can cause retention of the fluidity over extended time and can

5 achieve these results at low dosages. By manipulation of the conditions for the manufacture of the admixture, it is possible to obtain products that do not have an adverse effect on set retardation. Unlike lignosulfonates, the lignin-based admixtures of this invention are high in purity and free of sugar

10 contamination.

-6-

SUMMARY OF THE INVENTION

The invention provides for a novel lignin-based admixture produced from derivatized organosolv lignin. This lignin-based admixture uses a coproduct from an environmentally friendly process while fulfilling a need in the construction industry. The novel lignin-based admixture is produced by derivatizing organosolv lignin by treating the lignin in a sulfomethylation step. The derivatized lignin can be formulated with an air detrainer and the resulting admixture when added to concrete mixes effectively functions as a superplasticizer and as a high-range water reducer.

Novel features and aspects of the invention, as well as other benefits will be readily ascertained from the more detailed description of the preferred embodiments which follow.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The lignin which can be employed in this invention is a high purity lignin, particularly an organosolv lignin. The purity of the lignin in the present invention is from about 85% to about 100%. The lignin is separated as a by-product of the pulping and chemical delignification of plant biomass with organic solvents, for example ethanol. Organosolv lignin is a nontoxic, free-flowing powder. It is soluble in aqueous alkali and in selected organic solvents. It is generally characterized by its hydrophobicity, high purity, melt flow and a low level of carbohydrates and inorganic contaminants.

An example of the lignins which are suitable to accomplish the objectives of the invention are organosolv lignins such as regular ALCELL® lignin or low molecular weight ALCELL® lignin. The regular ALCELL® lignin can be characterized by a number average molecular weight of about 700 to 1500 g/mol and the low molecular weight ALCELL® lignin can be characterized

-7-

by a low average molecular weight in the range of less than 600 g/mol.

Alternatively to organosolv lignins, it is believed
5 that high purity lignins such as steam explosion or soda lignins can be suitable to accomplish the objectives of the invention.

The organosolv lignins of the invention can be derivatized using a sulfomethylation procedure. Before
10 carrying the sulfomethylation procedures described below, the lignin is solubilized into an alkaline solution. The amount of alkali used can vary depending on the type of lignin and the reaction conditions. For example, with ALCELL® lignin or low molecular weight ALCELL® lignin, from about 8% to about 20%
15 caustic based on lignin solids can be used. The amount of water used was adjusted to obtain a solids content in the final admixture of from about 30% to about 45%.

Before sulfomethylation, the molecular weight of the
20 lignin can be increased by crosslinking reactions. This can be accomplished by heating the lignin in alkaline solution for from about 1 to about 4 hours at from about 60°C to about 95°C. An alternative crosslinking approach consists in taking lignin in alkaline solution and reacting it with an aldehyde. When
25 formaldehyde is used, the reaction between the lignin and formaldehyde is a methylation reaction. The aldehyde can be added in a range of from about 0.3 to about 0.8 moles of aldehyde per lignin C-9 unit or of from about 5% to about 13% on a lignin weight basis. The methylation reaction can be carried
30 out at from about 60°C to about 95°C for from about 1 to about 3 hours.

A sulfomethylated lignin can be prepared in various alternative methods including the following. The lignin can be
35 reacted with a salt of hydroxymethane sulfonic acid such as its sodium salt. The latter is also known as "adduct" and is

-8-

available commercially. It is the addition product resulting from the reaction of formaldehyde with either sodium bisulfite or sodium sulfite. Preferably, the amount of adduct used for sulfomethylation can be from about 8% to about 30% adduct solids based on a weight basis with the lignin and the
5 sulfomethylation reaction time is from about 2 to about 6 hours. Sulfomethylation is generally performed at from about 70°C to about 100°C.

10 The lignin can also be sulfomethylated in a two-step process by initially reacting the lignin solution with excess of an aldehyde such as formaldehyde to methylolate the lignin thus introducing reactive aliphatic hydroxyl groups. This is done by following a similar procedure as described above to increase
15 molecular weight but using higher levels of aldehyde such as, for example, of from about 10 to about 30% formaldehyde on lignin weight. This methylation step is generally followed by reaction with from about 10 to about 25% sodium sulfite on a weight basis with lignin, at from about 120°C to about 160°C for
20 from about 1 to about 4 hours.

An alternative method to modify the molecular weight of the concrete admixtures of the present invention consists of crosslinking a sulfomethylated product with a crosslinking
25 agent such as epichlorohydrin. The epichlorohydrin can be added in a range from about 0.05 to about 0.5 moles of epichlorohydrin per sulfomethylated lignin C-9 unit or of from about 1.5% to about 16.5% on a sulfomethylated lignin weight basis. The crosslinking reaction can be carried out at from about 60°C to
30 about 100°C for from about 1 to about 4 hours.

The lignin-based admixtures can be mixed with a concrete mix in a range of from about 0.2% to about 1% on a weight basis with the cement in the concrete. The admixture
35 causes a water reduction of from about 5% to about 15% resulting

-9-

in higher concrete strength and improved resistance to freeze and thaw.

In certain applications, it may be desirable to control the entrained air in the resulting mix. An air detrainer such as tributyl phosphate, dibutyl phthalate, octyl alcohol, water-insoluble esters, carbonic and boric acids and silicones can be used. Tributyl phosphate (TBP) can be added to the derivatized lignin in a range of from about 0.3% to about 5% weight basis based on lignin solids resulting in a reduction in the air content of from about 9% to about 32% to as low as from about 2% to about 3% while maintaining reasonably high slump values.

15 Example I: Preparation of Sulfite Adduct

The adduct can be prepared by addition of about 60 grams of 50% formaldehyde to a solution of about 126 grams sodium sulfite in about 700 milliliters of water.

20

-10-

Example II: Manufacture of Admixtures

A series of lignin-based admixtures were prepared by sulfomethylation using as starting materials low molecular weight organosolv lignin, organosolv lignin and their methylolated counterparts. Initially, the lignins were dissolved in an aqueous solution of sodium hydroxide containing the alkali levels specified in Table 1. The amount of water used was adjusted to obtain a solids content in the final admixture of approximately 35% by weight. Those samples that were methylolated were treated with 0.5 moles of formaldehyde per lignin C-9 unit for 2 hours at 70°C. The sulfomethylation was carried out at a temperature of about 95°C and for 6 hours with adduct prepared as in Example I and using the levels described in Table 1.

Table 1

<u>Starting Lignin</u>	<u>Adduct</u>	<u>Sodium Hydroxide</u>
	(Mole per Lignin C-9 Unit)	
Low Molecular Weight	0.15	0.59
Low Molecular Weight	0.23	0.67
Low Molecular Weight	0.31	0.74
Methylolated Regular	0.15	0.67
Methylolated Regular	0.23	0.71
Methylolated Regular	0.31	0.78
Regular	0.15	0.58
Regular	0.23	0.66
Regular	0.31	0.73
Methylolated Low	0.15	0.55
Molecular Weight		
Methylolated Low	0.23	0.63
Molecular Weight		

-11-

Example III: Testing on Cement Slurries

The sulfomethylolated organosolv lignin-based admixtures were tested in cement slurries. The mixes were prepared by mixing together the following ingredients:

<u>Component</u>	<u>Dosage</u>
Portland Cement (Type 10)	5000 grams
Water	2250 grams
Admixture Solids	0.3% by weight on cement

Table 2 shows the initial set retardation on cement slurries. In general, the retardation decreases when the molecular weight increases and the level of adduct used decreases.

Table 2

	<u>Starting Lignin</u>	<u>Moles of Adduct per Lignin C-9 unit</u>		
		<u>0.15</u>	<u>0.23</u>	<u>0.31</u>
		<u>Set Retardation (min)</u>		
	Low Molecular Weight	200	380	380
	Regular	40	60	20
	Methylolated Low Molecular Weight	240	320	---
	Methylolated Regular	0	120	120

-12-

Table 3 shows the fluidifying effect of the lignin admixtures on cement slurries as determined by decrease in torque resistance. In general, lower molecular weight and high levels of adduct resulted in a greater fluidifying effect.

5 Table 3

Lignin Moles of Adduct per Lignin C-9 Unit

0.150.23 0.31

10

Torque Decrease (Nm)

	Low Molecular Weight	3.58	4.18	4.28
15	Regular	3.74	3.60	3.51
	Methylolated	2.95	4.06	---
	Low Molecular Weight			
	Methylolated	3.32	3.36	4.06
20	Regular			

Example IV: Preparation of Crosslinked Sulfomethylolated Lignins

25 Sulfomethylolated lignins were prepared using as starting materials low molecular weight organosolv and organosolv lignin as outlined in Example II. The sulfomethylation reaction took place at a temperature of about 95°C and for about 6 hours using the levels described in Table

30 4. The regular sulfomethylolated organosolv lignin was further crosslinked by reacting the sulfomethylolated lignin with 12.6% by weight of epichlorohydrin at about 95°C for 140 minutes. Upon cooling, the resulting solution had a pH of 11.89, contained 41% solids by weight and had a viscosity of 3,600 cps.

-13-

Table 4

	<u>Starting Lignin</u>	<u>Adduct</u> (% on a lignin weight basis)	<u>Sodium Hydroxide</u>
5			
	Low molecular weight	16.1%	12.0%
	Regular	36.8%	20.5%

10

Example V. Testing on Cement Slurries

The crosslinked sulfomethylolated lignins in Example IV were incorporated into cement slurries in the quantities set forth in Example III (with the exception of the fact that only 1,750 grams of water were used in this case) and the slurries were tested for torque decrease and set retardation. The results of those tests are provided in Table 5.

15

Table 5

20

	<u>Lignins</u> (min)	<u>Torque Decrease (Nm)</u>	<u>Set Retardation</u>
	Low molecular weight	29.9	330
25	Regular after crosslinking with epichlorohydrin	28	130

Table 5 shows that the admixture obtained after crosslinking the regular sulfomethylolated lignin with epichlorohydrin had approximately the same fluidity (torque decrease) as the low molecular weight sulfomethylolated product, but had considerably less set retardation.

30

-14-

Example VI: Testing on Concrete Mixes

Sulfomethylolated low molecular weight lignin obtained with a ratio of 0.31 moles per lignin C-9 unit using the procedure of Example II was evaluated as an admixture in concrete mixes. The effect of tributyl phosphate as an air entrainer agent was also evaluated. The proportions of the concrete mixes were as follows:

10	<u>Component</u>	<u>Dosages (kg/m³)</u>
	Portland Cement (Type 10)	307
	Fine Aggregate	862
	Coarse Aggregate	935
15	Water	187
	Admixture	4.87 (0.5% solids on a weight basis with cement)

The proportion of cement in the mixes conformed to the requirements of ASTM specification C-494.

Table 6 demonstrates the beneficial plasticizing effect of the low molecular weight sulfomethylolated organosolv lignin of Example VI on concrete mixes as shown by the high slump numbers of such mixes relative to a concrete mix containing no admixture; see the first entry of Table 6. The second entry of that table further reveals that if an air detrainer is not used, a high air content can be observed which causes a decrease in concrete strength. Tributyl phosphate (TBP) can be added to reduce the air content while maintaining a high slump and high strength. As can be seen in the third through fifth entries, by adjusting the amount of detrainer agent added, a wide variety of air contents can be attained, including air contents for non-air entrained concrete (below 3.5%) and air contents for typical air entrained concrete of 4 to 8%.

-15-

Table 6

	Low Molecular weight sulfomethylolated lignin (% solids based on cement)	Tributyl phosphate	Air content %	Slump mm	Compressive strength MPa
5					
10	0	0	2.5	40	37.77
	0.5	0	25.5	155	11.31
	0.5	2	5.0	155	35.82
	0.5	3	3.0	110	37.3
	0.5	4	4.0	120	37.1

15

Example VII:

In this example, sulfomethylolated low molecular weight organosolv lignin of Example VI formulated with an air detrainer showed a higher plasticity over a commercial lignosulfonate such as PDA-25XL from Conchem. The results are shown in Table 7.

25 Table 7

	Admixture	Air Content (%)	Slump (mm)
25			
30	Control	2.5	40
	Sulfomethylolated low molecular weight ALCELL® lignin + 4% TBP on lignin solids	2.5	120
35	Commercial lignosulfonate based admixture	2.5	85

-16-

Example VIII:

5 In this example, a low molecular weight lignin-based
admixture prepared as in Example II with a 0.31 moles of adduct
per lignin C-9 unit and an air-entrained reference mix were
subjected to superplasticizing admixture qualification tests.
The admixture contained about 1.5% TBP as an air detrainer. The
10 reference mix was prepared without the superplasticizer
admixture and included 147mL of air entraining agent per m³. The
following concrete mix proportions were used.

-17-

<u>Component</u>	<u>Dosages (per m³)</u>	
	<u>Non-Air-Entrained</u>	<u>Air-Entrained</u>
5 Portland Cement (Type 10)	307 Kg	307 Kg
Fine Aggregate	734 Kg	694 Kg
Coarse Aggregate	1150 Kg	1128 Kg
Water	175 Kg	160 Kg
10 Admixture 4 L (at 35% solids)	4 L	---
Air Entraining Admixture	None	362 mL

15 The mixing procedure was in accordance with CSA
Standard CAN3-A266.6-M85. Fresh concrete was tested for
workability by measuring the slump in accordance with ASTM
specification C-143-90a. The time of setting was determined by
measuring the penetration resistance on mortar extracted from
20 the concrete mixture in accordance with ASTM specification C403-
92. The compressive strength of hardened concrete was measured
in accordance with ASTM specification C-192-90a, ASTM
specification C-39-86 and ASTM specification C-617-87. Length
change was measured in accordance with CAN/CSA-A23.2-3C and
25 CAN/CSA-A23.2-14A. Durability factor was calculated from
relative dynamic modulus of elasticity changes in concrete
prisms exposed to repeated cycles of freezing and thawing in
accordance with ASTM specification C666-92.

30 Table 8 is a summary of the superplasticizing
admixture qualification tests for the non-air-entrained and the
air-entrained reference mix compositions.

-18-

Table 8

	Concrete property	Non-Air	Air	CSA/CANS
		Entrained	Entrained	A266.6-M85
5		Concrete	Concrete	Type SPR
	Water content,			
	% of reference	87	87	max. 88
	Slump retention, %	76	63	min. 50
	Time of initial			
10	set retardation			
	h:min	2:40	2:45	1:00 to 3:00
	Compressive strength,			
	% of ref x 1.05 (CSA)			
	1 day	137	150	min. 130
15	3 days	131	155	min. 130
	7 days	143	142	min. 125
	28 days	124	137	min. 120
	180 days	130	145	min. 100
20	Length Change			
	(shrinkage) % of	119	106	max. 135
	ref. or increase			
	over reference	0.005	0.002	max. 0.010
	Relative durability			
25	factor	not required	109/99	min. 100
	% of ref. x1.1 (CSA)			

When the length change of the reference concrete is
 30 0.030% or greater % of reference limit applies; increase over
 reference limit applies when length change of reference is less
 than 0.030%.

As can be observed, the admixture invariably met the
 35 requirements of the superplasticizing standards and resulted in
 concrete with higher strength than the reference. Hence,

-19-

admixtures formulated in accordance with the present invention can be classified as a superplasticizer.

Example IX: Testing on Concrete Masonry Blocks

5

Sulfomethylolated low molecular weight lignin with 35% solids content by weight was tested in concrete blocks production, both as a water reducer and as replacement for an air entrainer agent. Each mix was prepared with 172 kg of cement and 1814 kg of fine aggregate. The amount of water per mix was adjusted to obtain the desired workability of concrete. The admixture and quantities were as follows:

15	Admixture	Quantity (mL)
	Control	Airex L 120
	Mix 1	Sulfomethylolated 1500
20		Low Molecular Weight
		Lignin + 1.2% TBP
	Mix 2	Sulfomethylolated 750
		Low Molecular Weight
		Lignin
25	Mix 3	Sulfomethylolated 1500
		Low Molecular Weight
		Lignin
	Mix 4	Sulfomethylolated 2000
		Low Molecular Weight
30		Lignin
	Mix 5	Sulfomethylolated 3000
		Low Molecular Weight
		Lignin

35

-20-

A total of 110 standard hollow masonry units (blocks) were prepared from each concrete mix. All blocks were prepared and cured using standard procedure. Subsequently a randomly chosen sample from each batch was tested for compressive strength. Table 9 summarized the results of testing of standard hollow concrete masonry units. As can be seen, the use of the lignin-based admixtures of the invention resulted in higher strength. In general, as the admixture level increases, the concrete strength increases.

Table 9

Concrete Mix	Block Age (days)	Gross Stress (%)
Control	8	100
Control	15	100
Mix 1	8	115
Mix 2	15	98
Mix 3	15	107
Mix 4	15	108
Mix 5	15	118

The invention and many of its attendant advantages will be understood from the foregoing description, and it will be apparent that various modifications and changes can be made without departing from the spirit and scope of the invention or sacrificing all of its material advantages, the compositions and processes hereinbefore described being merely preferred embodiments.

-21-

We claim:

1. An admixture for reducing the water content of a concrete mix comprising an alkaline solution of a lignin in a range of from about 30% to about 45% on a solids weight basis with said lignin solution.

2. The admixture of claim 1 wherein said lignin is in sulfomethylolated form.

3. The admixture of claim 2 wherein said lignin has a purity from about 85% to about 100%.

4. The admixture of claim 2 further comprising an air detrainer.

5. The admixture composition of claim 4 wherein said air detrainer is tributyl phosphate.

6. The admixture of claim 5 wherein said air detrainer is from about 0.3% to about 5% on a weight basis with said lignin.

7. The admixture of claim 2 wherein said sulfomethylolated lignin is crosslinked with a crosslinking agent.

8. The admixture of claim 7 wherein said crosslinking agent is epichlorohydrin.

9. The admixture of claim 8 wherein said epichlorohydrin is in a range of from about 1.5% to about 16.5% on a sulfomethylolated lignin weight basis.

10. A cement composition comprising a cement and an admixture for reducing the water content of said cement

-22-

composition, said admixture in a range of from about 0.2% to about 1% on a solids weight basis with said cement

11. The composition of claim 10 wherein said admixture
5 comprises an alkaline solution of a lignin in a range of from about 30% to about 45% on a solids weight basis with said lignin solution.

12. The composition of claim 11 wherein said lignin is
10 in sulfomethylolated form.

13. A concrete masonry block comprising the composition of claim 12.

14. The composition of claim 12 wherein said lignin
15 has a purity from about 85% to about 100%.

15. The composition of claim 12 wherein said admixture
comprises an air detainer.

20

16. The composition of claim 15 wherein said air
detainer is tributyl phosphate.

17. The composition of claim 16 wherein said air
25 detainer is from about 0.3% to about 5% on a weight basis with said lignin.

18. The composition of claim 12 wherein said
sulfomethylolated lignin is crosslinked with a crosslinking
30 agent.

19. The composition of claim 18 wherein said
crosslinking agent is epichlorohydrin.

-23-

20. The composition of claim 19 wherein said epichlorohydrin is in a range from about 1.5% to about 16.5% on a sulfomethylolated lignin weight basis.

5 21. A method for reducing the water content of a cement mix comprising the step of adding an admixture to said concrete mix in a range of from about 0.2% to about 1% on a solids weight basis with said cement.

10 22. The method of claim 21 wherein said admixture comprises an organosolv lignin.

 23. The method of claim 22 wherein said organosolv lignin is in sulfomethylolated form.

15 24. The method of claim 23 wherein said organosolv lignin has a purity from about 85% to about 100%.

 25. The method of claim 23 wherein said admixture
20 further comprises an air detainer.

 26. The method of claim 25 wherein said air detainer is tributyl phosphate.

25 27. The method of claim 26 wherein said air detainer is from about 0.3% to about 5% on a weight basis with said lignin.

 28. The method of claim 23 further comprising
30 crosslinking said sulfomethylolated lignin with a crosslinking agent.

 29. The method of claim 28 wherein said crosslinking agent is epichlorohydrin in a range from about 1.5% to about 16.5% on a sulfomethylolated lignin weight basis.

35

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)